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Computational Studies of Ionic Liquids

AFOSR Ionic Liquids Workshop

March 7-8, 2004

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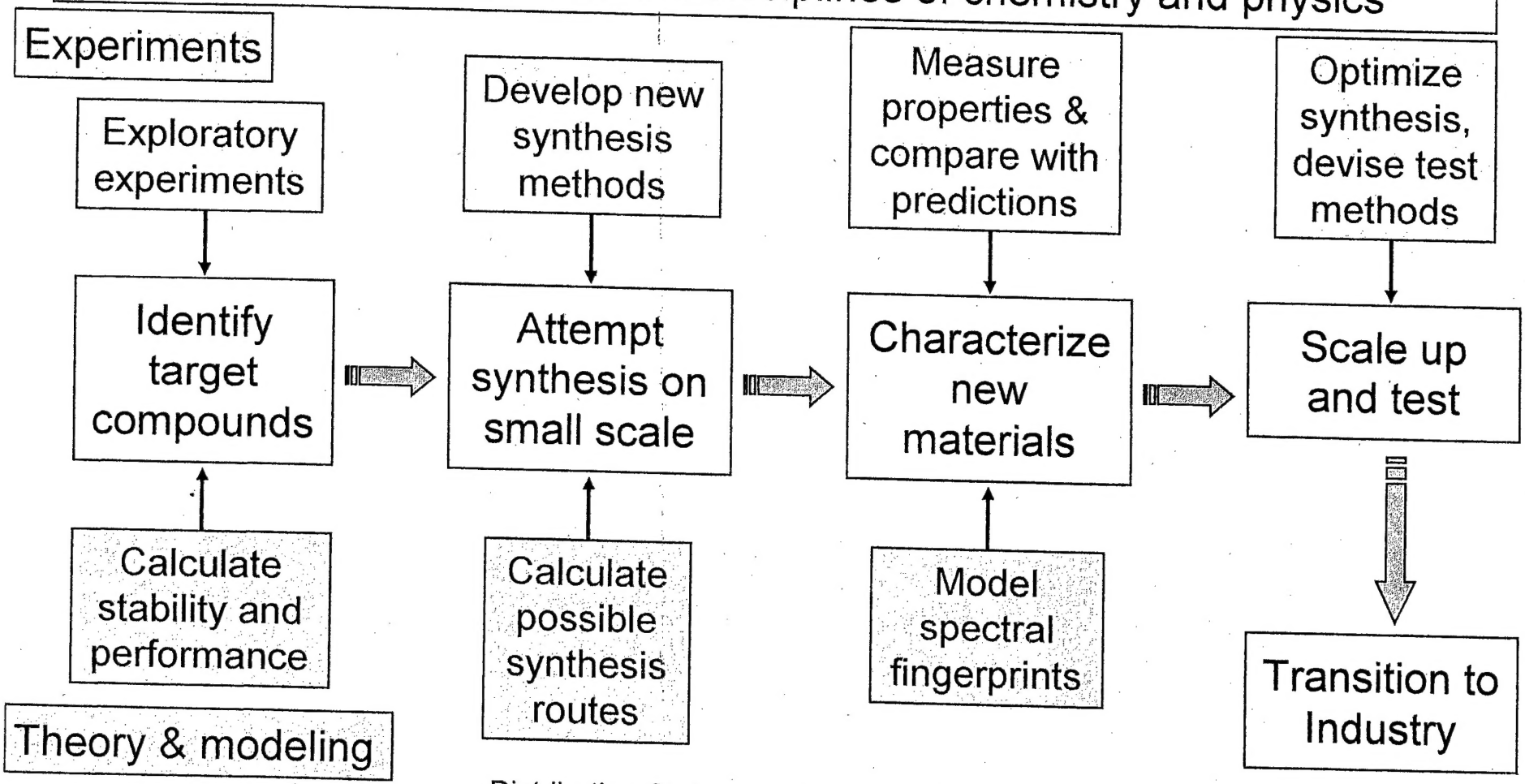
Outline

1. Introduction
2. Structures and relative energies of 1,5-diamino-1,2,3,4-tetrazolium cation
3. Summary and Conclusions

Propellants Program General Approach

Employ a synergic blend of experimental, theoretical, and computational techniques derived from the disciplines of chemistry and physics



Modeling & Simulation of New Chemical Propellants

Various computational techniques are employed to solve the molecular electronic Schrödinger equation from quantum mechanics:

$$\left[-\frac{1}{2}\sum_i \nabla_i^2 - \sum_i \sum_\alpha \frac{Z_\alpha}{r_{i\alpha}} + \sum_i \sum_{j>i} \frac{1}{r_{ij}}\right]\Psi_{el} = E_{el}\Psi_{el}$$

Is a proposed propellant molecule/material stable?

Structure optimization, verification as local minimum

What is its energy content?

Heats of formation and combustion

How may it be synthesized? How will it react/decompose/combust?

Reaction pathways

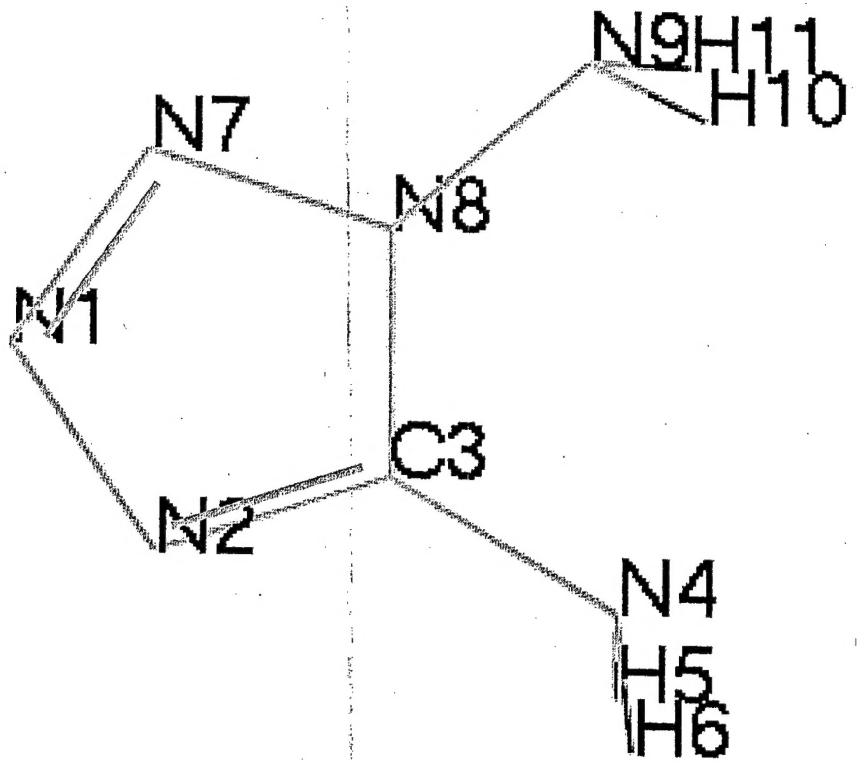
How will we know if we've synthesized it?

Vibrational spectra (IR, Raman, isotopic shifts)
NMR chemical shifts
Electronic spectra

1,5-diamino-1,2,3,4-tetrazole

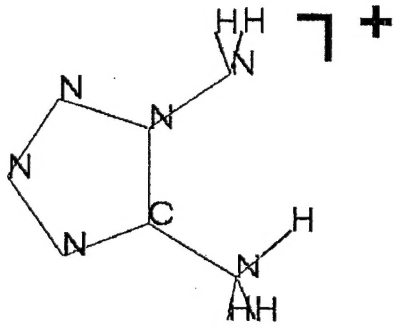
What is the preferred N-protonation site?

What level of theory is required?



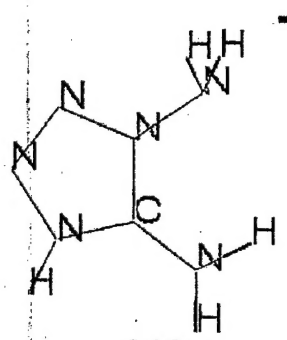
B3LYP(3) Structures and Relative Energies (kcal/mol)

B3LYP(3)/6-311G(d,p) [B3LYP(3)//aug-cc-pvtz//B3LYP]



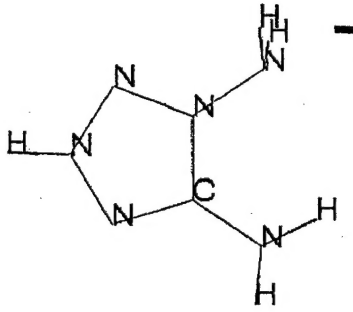
1 (C_s)

35.5 [36.6]



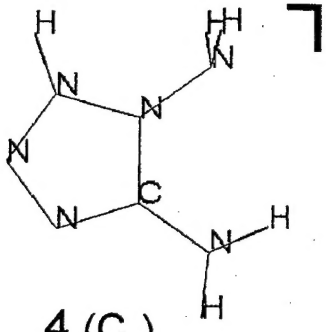
2(C_s)

2.1 [3.2]



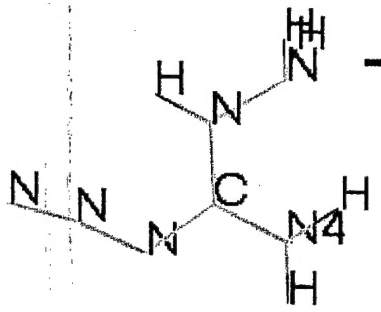
3 (C_s)

5.0 [5.6]



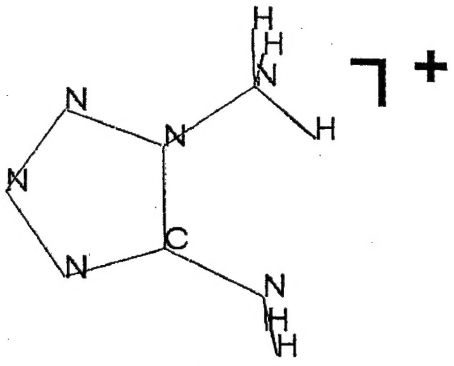
4 (C_s)

18.0 [18.6]



5(C_s)

0.0 [0.0]

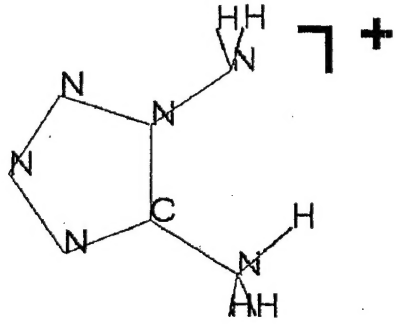


6 (C_S)

42.9 [43.9]

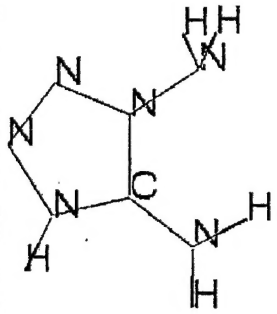
MP2 Structures and Relative Energies (kcal/mol)

MP2/6-311G(d,p) [CCSD(T)/6-311G(2df,p)//MP2]



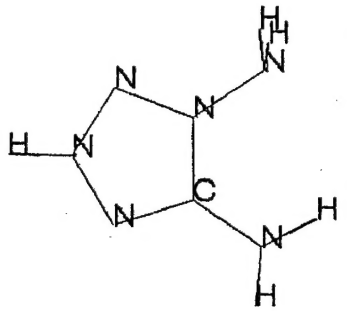
1 (C_s)

26.9 [29.6]



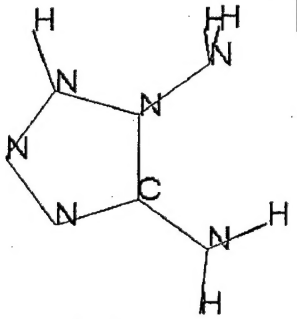
2(C_1)

0.6 [0.0]



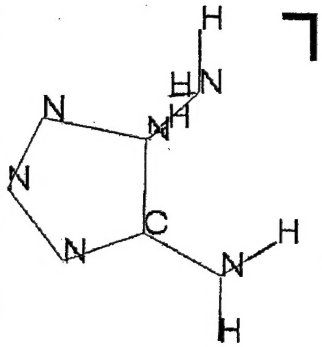
3 (C_1)

0.0 [3.3]



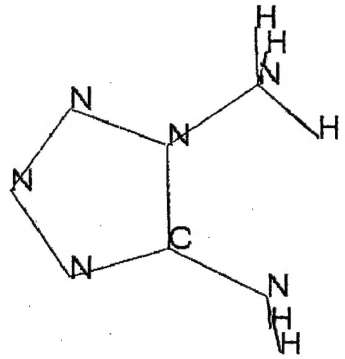
4 (C_1)

18.7 [16.8]



2(C_1)

51.2 [45.6]



3 (C_S)

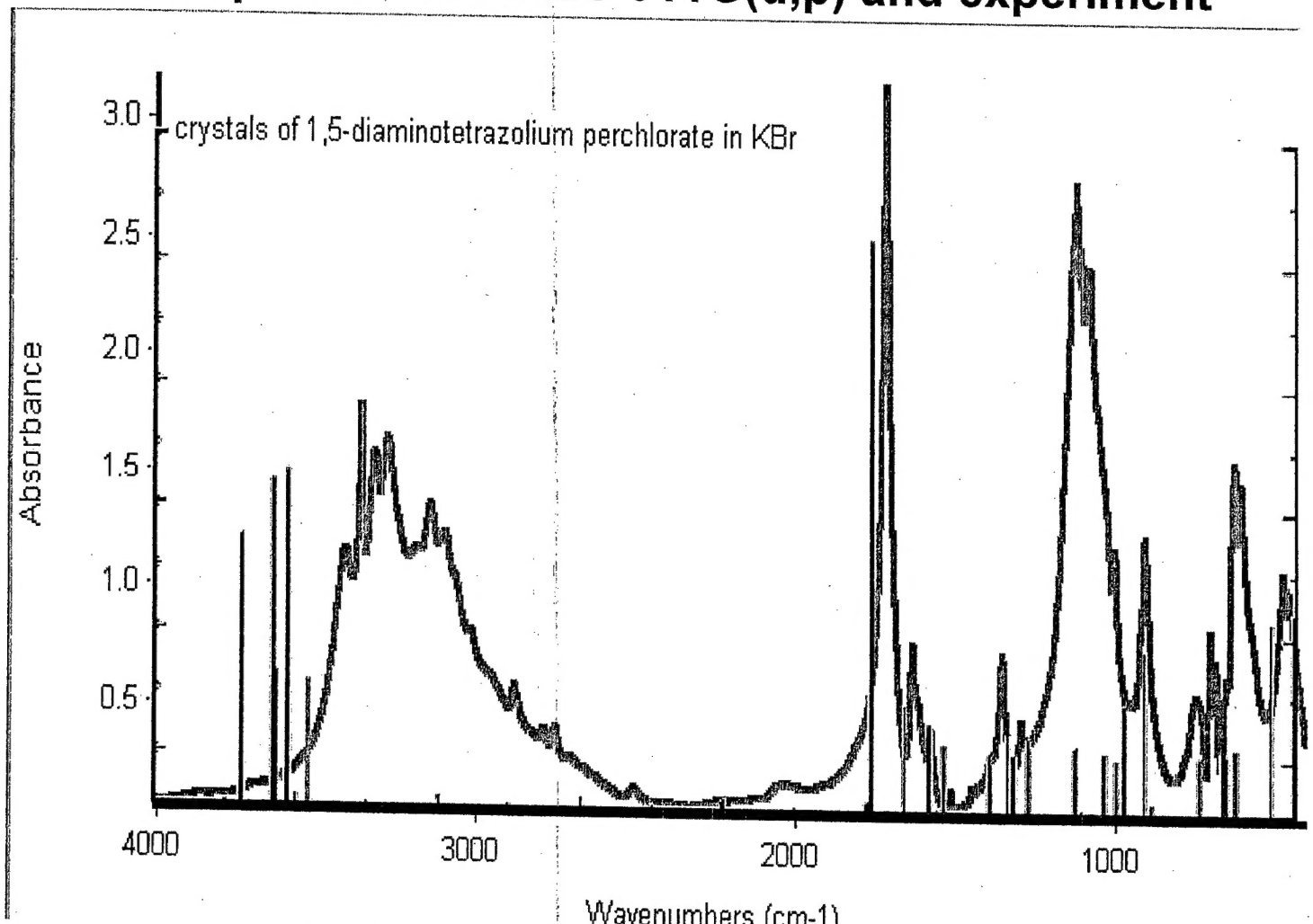
36.4 [38.0]

Summary of Relative Energies (kcal/mol)

	1	2	3	4	5	6
B3LYP(3)/6-311G(d,p)	35.5	2.1	5.0	18.0	0.0	42.9
B3LYP(3)/6-311G(2df,p)//	---------- TBD ----------					
B3LYP(3)/aug-cc-pvtz//	36.6	3.2	5.6	18.6	0.0	43.9
MP2/6-311G(d,p)	26.9	0.6	0.0	18.7	51.2	36.4
MP2/6-311G(2df,p)//	---------- TBD ----------					
MP2/aug-cc-pvtz//	---------- TBD ----------					
CCSD(T)/6-311G(2df,p)//MP2	29.6	0.0	3.3	16.8	45.6	38.0

Infrared Vibrational Spectra

Comparison of MP2/6-311G(d,p) and experiment



Summary & Conclusions

- The structures and relative energies of the six possible N-protonated structures of the 1,5-diamino-1,2,3,4-tetrazolium cation have been computed at the B3LYP(3)/6-311G(d,p) and MP2/6-311G(d,p) levels of theory. Relative energies have been refined at the B3LYP(3), MP2, and CCSD(T) levels, using the 6-311G(2df,p) and aug-cc-pvtz basis sets.

- Isomers 2 (4H) and 3 (3H) are essentially degenerate at all levels of theory.

- B3LYP predicts isomer 5 (1H) to ring open to form an azide ($NH_2NHC(N_3)=NH_2$.

- CCSD(T)/6-311G(2df,p)//MP2/6-311G(d,p) calculations predict structure 2 to be the most stable isomer, in agreement with the X-ray crystal structure of the perchlorate salt.

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